

Commonwealth of Kentucky
Division for Air Quality
PERMIT STATEMENT OF BASIS

Draft Title V / Synthetic Minor, Construction / Operating

Permit: V-06-052

ISP Chemicals, LLC

Calvert City, KY 42029

June 22, 2007

Carolina Alonso, Reviewer

SOURCE ID: 21-157-00003

SOURCE A.I. #: 2939

ACTIVITY ID: APE20060003

SOURCE DESCRIPTION:

ISP Chemicals Inc. (ISP) is a large Synthetic Organic Chemical plant that makes a wide variety of intermediates and specialty chemicals. The source is a major source, as defined by 401 KAR 52:020 Title V Permits, for the potential emissions of over 100 tons per year of sulfur dioxide (SO₂), nitrogen oxides (NO_x), carbon monoxide (CO), and volatile organic compounds (VOC), the potential of a single hazardous air pollutant (HAP) greater than 10 tons per year, and the potential combined HAP emissions greater than 25 tons per year.

The source is also a major source, as defined by 401 KAR 51:017 Prevention of Significant Deterioration of Air Quality (PSD), for potential emissions of over 100 tons per year of SO₂, NO_x, CO and VOC.

ISP is renewing a sourcewide Title V permit issued on April 12, 2002. For the purpose of Title V permitting, this facility is split into the following areas:

1. **Gamma-butyrolactone (BLO) unit:** BLO is produced by vapor phase dehydrogenation of butanediol in a fixed-bed catalytic reactor. Crude BLO is distilled, purified, cooled, and stored. High boiling residues are removed as non-hazardous waste and shipped off-site for Btu recovery. Lights are sent to the comparable fuels tank for subsequent Btu recovery in ISP's boilers. By-product hydrogen is vented to the boilers for Btu recovery, or vented to the atmosphere. Wastewater is sent to the on-site wastewater treatment plant.
2. **Pyrrolidones unit:** 2-Pyrrolidone is produced by the reaction of anhydrous ammonia and BLO. The crude product is sent to a distillation unit, BLO is also reacted with an alkylamine to form a substituted pyrrolidone. Crude product is cooled and distilled in Area 315, or Area 211, or sent to a toll processor.
3. **Vinyl Pyrrolidone unit:** Vinyl Pyrrolidone (VP) is produced by reacting 2-pyrrolidone with acetylene. Potassium hydroxide is used as a catalyst. Propane is used as an inert diluent. The crude VP is purified by distillation, and unreacted 2-pyrrolidone is recycled to the reactor. Some VP is stabilized and stored in tanks. The balance of the VP is used to make other products downstream of this process.
4. **Solvent recovery unit:** The distillates from the Gantrez ES-225 and ES-425 processes are

separated into acetone and ethanol. Purge streams containing alcohols and ketones are combined and used in the boilers as comparable fuels. Ethanol is re-used in the Gantrez process.

5. **Methyl vinyl ether unit:** Acetylene is purified, mixed with methanol vapor, and fed to the reactor (vinylator). The catalytic reaction produces crude methyl vinyl ether (MVE), which is then purified, condensed, washed, and dried. MVE is reclaimed by removing the contaminant acetaldehyde. Since production of virgin MVE and MVE reclamation use some of the same equipment, the two processes cannot currently run simultaneously.
6. **Storage tanks**
7. **200 Building:** The 200 building is used to produce several products, each with many grades. Several grades of alkylated polyvinylpyrrolidone (Ganex) are produced by charging the reactor with VP, an olefin, an initiator, and alcohol as a diluent. After the reaction, the batch is cooled. When the desired solids content of the batch is achieved, the product is filtered, cooled, and packaged. Several grades of Polyvinylpyrrolidones (PVP) are produced by batch polymerization of N-Vinyl-2-Pyrrolidone (VP).
8. **236 Building:** Many different batch processes are conducted in the 236 building. The 236 building also uses some materials produced in the 240 building. Solution products are shipped out via tank trucks or drums. Dried products are packaged in drums or totes.
9. **240 Building:** Building 240 produces copolymers of maleic anhydride (MA), methyl vinyl ether (MVE), isobutylene, and isopropyl acetate. The reactions use various proportions of reactants, solvents, and initiators. Product slurry is generated in the four reactors, stripped of un-reacted monomer (if needed) in the stripping tanks, and then pumped to holding tanks that feed into the three product dryers. Dried powder is mixed in six blenders, and packaged into drums, totes, super sacks, or air pallets. Some reactor products are not dried, but are transferred to tanks for storage or transferred directly to downstream processes.
10. **315 Building:** In the 315 building copolymers of PVP are produced. VP and a solvent are charged to the reactor. The remaining amounts of VP and solvent are added followed by the initiator. When the monomer concentrations are below the specifications, the batch is cooled. The solids are adjusted after mixing with an additive. The product is then loaded into drums. Gafquats are produced when VP is copolymerized with various organic salts in presence of an initiator. Water or ethanol is typically used as a solvent. The solids are adjusted, filtered, and the final product is packed into drums. Batch products other than the above vinyl pyrrolidone-based products are also made in the 315 building. Solution products are shipped out via tank trucks and drums. Dried products are packaged in drums or totes.
11. **Higher vinyl ethers (HVE) unit (326 area):** A variety of high molecular weight vinyl ethers are produced in a batch process in the 326 Area. Raw materials are heated to reflux in a prep kettle. Using the prep kettle vacuum, a solution of potassium hydroxide (KOH) is drawn into the kettle from the melt pot. The reaction occurs by sparging a mixture of acetylene / propane through the batch. Unreacted gas from the top of the reactor is released through a cooler to a buffer tank where acetylene / propane is added. Vapors from the gas in the cooler are separated and returned to the reactor. The batch is then transferred to the degasser, where residual acetylene / propane is removed by sparging with nitrogen. After sparging, the degasser is discharged either

to the unit, a tank wagon, or to drums.

12. **334 Building:** PVP-I is prepared in the 334 building by reacting iodine prills with PVP powder. The reaction occurs at controlled conditions in a tumbler mixer to form an iodide complex in the presence of water. The slurry is then spray dried and packaged into drums.

13. Wastewater treatment

14. Utilities / R&D

The renewal application includes the following projects:

- Construction of new reactor and dryer in 240 Building. Since uncontrolled emissions are over 40 tpy for VOC, the facility has accepted operating limits to preclude applicability of PSD.
- East Paracymene heater will be modified to burn hydrogen and increase capacity to 15 mmBtu/hr. The modification will trigger applicability of 40 CFR 60 Subpart Dc and 401 KAR 59:010 for this heater.
- ISP is planning on replacing the existing wastewater treatment plant with a new, more efficient plant. The new plant and conveyance system will have much lower emissions than the current system, but emissions from the project will be greater than 40 tpy. A netting analysis was performed (see following table). The net emissions increase is -94.29, so PSD review will not be required for this project.

VOC Net Emissions Increase for WWT Plant Re-Build Contemporaneous Period from October 2001 through June 2007

Date Change Commenced	Construction, Reconstruction, Modification	Submitted to DAQ	Baseline Actual VOC (ton/yr)	Future VOC Emissions (ton/yr)	Emissions Change (ton/yr)	Comments
1/1/2002	Installation of cyclohexylamine storage tank 311/3006	7/30/2001	0	0.05	0.05	Future potential emissions from July 30, 2001 off-permit change notification
1/1/2002	Installation of dodecylamine storage tank 311/3007	7/30/2001	0	6.61E-03	6.61E-03	Future potential emissions from July 30, 2001 off-permit change notification
9/30/2002	Addition of tank 313/3006 for vinyl caprolactam crude service	4/19/2002	0	2.00E-05	2.00E-05	Future potential emissions from April 19, 2002 section 502(b)(10) notification
11/1/2003	H2 combustion in wickes boiler	9/16/2003	0	1.90	1.90	Past actual conservatively assumed to be zero. Future potential from September 16, 2003 minor permit revision application at continuous gas/hydrogen combustion
4/23/2004	Recommission tank 311/3009 intended for ethanol service	3/23/2004	0	0.22	0.22	Future potential emissions from March 23, 2004 off-permit change notification

Date Change Commenced	Construction, Reconstruction, Modification	Submitted to DAQ	Baseline Actual VOC (ton/yr)	Future VOC Emissions (ton/yr)	Emissions Change (ton/yr)	Comments
8/14/2005	Installation of R&D pilot plant	7/14/2005	0	6.0	6.0	Future potential emissions from July 14, 2005 minor permit revision application
2006	Remove scrubber 311/5301 from cyclohexylamine tank 311/3006	10/6/2006	0	0.05	0.05	Baseline actual conservatively assumed to be zero. Future potential from October 6, 2006 Title V renewal application.
2006	Remove scrubber 311/5302 from monoethylamine tank 311/3008	10/6/2006	0	8.00E-04	8.00E-04	Baseline actual conservatively assumed to be zero. Future potential from October 6, 2006 Title V renewal application.
2006	Remove scrubber 242/5302 for maleic anhydride tank 242/3101	10/6/2006	0	0.03	0.03	Baseline actual conservatively assumed to be zero. Future potential from October 6, 2006 Title V renewal application.
2006	Remove scrubber 305/5301 for diethyl sulfate tank 305/3101	10/6/2006	0	3.60E-04	3.60E-04	Baseline actual conservatively assumed to be zero. Future potential from October 6, 2006 Title V renewal application.
2006	Disconnect Gantrez Scrubber 236/5375 from Drum Dryer 236/3506	10/6/2006	0	36.00	36.00	Baseline actual conservatively assumed to be zero. Future predicted actual from October 6, 2006 Title V renewal application.
2006	Use of existing 224 and 225 BLO columns to distill pyrrolidones	10/6/2006				Emissions reduction - no credit taken
2007	Modification of E Paracyemene heater to burn hydrogen and increase capacity to 19 mmBtu/hr	10/6/2006	0	0.44	0.44	Baseline actual conservatively assumed to be zero. Future potential from October 6, 2006 Title V renewal application adjusted to reflect 19 MMBtu/hr rating versus 15 MMBtu/hr originally proposed.
2007	Addition of new 236/32xx product receiver for HEG - acetone and MVE service - 9,000 gal capacity	10/6/2006	0	4.50	4.50	Future potential from October 6, 2006 Title V renewal application.
2007	Increase size of maleic anhydride tank 242/3101 to 9,000 gal	10/6/2006	0	0.03	0.03	Baseline actual conservatively assumed to be zero. Future potential from October 6, 2006 Title V renewal application.
2007	Use of existing 211 columns to increase BLO production rate	5/1/2007	9.67	23.51	13.84	Baseline actual and future predicted actual from May 2007 Minor Permit Revision application.
Jun-07	Convert WWT collection system from ditches to hard-piping	10/6/2006	14.30	10.06	-4.24	Baseline actual from April 1996 Radian report, adjusted to reflect 2004-2005 configuration. Future potential from URS October 2006 Water9 report.
Jun-07	Shutdown of existing WWT system	10/6/2006	206.81	0.00	-206.81	Baseline actual from Water9 calculations
Jun-07	New WWT system	10/6/2006	0.00	53.69	53.69	Future potential from URS October 2006 Water9 report. Includes new WWT system and sump overflow malfunctions

Date Change Commence d	Construction, Reconstruction, Modification	Submitted to DAQ	Baseline Actual VOC (ton/yr)	Future VOC Emissions (ton/yr)	Emissions Change (ton/yr)	Comments
Net Emissions Increase					-94.29	

There are also several off-permit changes and minor revisions.

MINOR PERMIT REVISION FOR the Reclaim MVE Project:

An additional washer/dryer will be added to the Methyl Vinyl Ether (MVE) process. Annual potential VOC emissions have been estimated not to be greater than 75.3 ton/yr, the emissions increase will be less than 40 ton/yr PSD significance level for VOC so no emission limits are necessary to preclude applicability of PSD.

MINOR PERMIT REVISION FOR use of B3D flare:

Previously out-of-service B3D flare will be used for odor control.

MINOR PERMIT REVISION FOR the addition of product receiver:

A new 9,000 gallon product receiver will be installed in the 236 Building, intended for HEG-acetone and MVE service.

MINOR PERMIT REVISION FOR the addition of maleic anhydride tank:

A new 11,500 gallon maleic anhydride tank will be installed.

MINOR PERMIT REVISION FOR filter feed tanks:

Polymer transfer to filter feed tanks 236/3311 and 236/3312. These tanks are incorporated to Section C - Insignificant Activities.

MINOR PERMIT REVISION FOR disconnecting scrubber:

Gantrez scrubber 236/5375 will be disconnected from Drum Dryer 236/3506.

MINOR PERMIT REVISION FOR using BLO 224 and 225 in Pyrrolidones unit:

Existing BLO 224 and 225 columns will be used to distill Pyrrolidones. VOC emissions will decrease.

MINOR PERMIT REVISION FOR the BLO Parallel Towers Project:

ISP is planning on tying in existing area columns 211/3411 and 211/3415 to the existing BLO unit. Future projected actual process emissions are 23.51 tpy of VOC, the emissions increase will be less than 40 ton/yr PSD significance level for VOC so no emission limits are necessary to preclude applicability of PSD.

COMMENTS:

Applicable Regulations:

The source is subject to the following regulations:

401 KAR 51:017. *Prevention of Significant Deterioration of Air Quality.*
401 KAR 59:010. *New Process Operations* constructed after July 2, 1975.
401 KAR 59:015. *New Indirect Heat Exchanger* constructed after April 9, 1972.
401 KAR 61:015. *Existing Indirect Heat Exchangers* constructed prior to April 9, 1972.
401 KAR 61:020. *Existing Process Operations* constructed prior to July 2, 1975.
401 KAR 63:010. *Fugitive Emissions.*
401 KAR 63:015. *Flares.*

40 CFR 60 Subpart Dc. *Standards of performance for small industrial-commercial-institutional steam generating units that commences construction, modification, or reconstruction after June 9, 1989.*

40 CFR 61 Subpart J. *National Emission Standard for Equipment Leaks (Fugitive Emission sources) of Benzene.*

40 CFR 61 Subpart V. *National Emission Standard for Equipment Leaks (Fugitive Emission Sources.)*

40 CFR 61 Subpart Y. *National Emission Standard for Benzene Emissions from Benzene Storage Vessels.*

40 CFR 61 Subpart FF. *National Emission Standard for Benzene Waste Operations.*

40 CFR 64. *Compliance Assurance Monitoring (CAM)*, applies to the Riley boiler and the 200 Gas Spray Dryer for particulate matter.

40 CFR 63 Subpart FFFF - *National Emission Standards For Hazardous Air Pollutants: Miscellaneous Organic Chemical Manufacturing* applies sourcewide.

40 CFR 63 Subpart EEEE - *National Emission Standards For Hazardous Air Pollutants: Organic Liquid Distribution (Non-Gasoline)* applies to some storage tanks and transfer racks.

40 CFR 63 Subpart GGGGG - *National Emission Standards For Hazardous Air Pollutants: Site Remediation.*

Non-Applicable Regulations:

40 CFR 63 Subpart DDDDD, *National Emission Standards for Hazardous Air Pollutants for Industrial, Commercial, and Institutional Boilers and Process Heaters* was vacated and remanded by U.S. Court of Appeals on July 30, 2007. The facility will be required to perform a case-by-case MACT analysis, if notified to do so.

Emission Factors:

Emission factors are mainly calculated using the Emissions Master database (ISP's software). Boilers emissions are based on AP-42 factors.

EMISSION AND OPERATING CAPS DESCRIPTION:

In order to preclude applicability of 401 KAR 51:017, Prevention of Significant Deterioration of Air Quality (PSD), the source has elected to accept the following limits:

Area	Equipment	Limit Description	Pollutant
BLO	BLO process unit	The permittee shall calculate and maintain a record of actual process vent emissions, in tons per year on a calendar year basis, of VOC from the BLO process unit.	VOC
240 Building	Reactor 5 and Dryer 4	Emissions shall not exceed 36 ton/yr.	VOC
236 Building	Drum Dryer 236/3506	Actual emissions shall not exceed 36 ton/yr.	VOC
Zurn Boiler	Zurn Boiler	No. 2 Fuel Oil use shall not exceed 700,000 gal/yr.	SO ₂
Zurn Boiler	Zurn Boiler	Emissions shall not equal or exceed 36 ton/yr.	SO ₂

PERIODIC MONITORING:

PM/PM10 controls include a cyclone, baghouses, and scrubbers. Periodic monitoring consists of routine maintenance, monitoring of pressure drops, and periodic visual observations.

The source has a thermal oxidizer to control emissions of benzene from the storage vessels 242/3001, 3002, and 3005 to meet the requirements of 40 CFR 61 Subpart Y. Refer to permit V-06-052 for specific monitoring requirements. The source has submitted the Operating Plan for Carbon Canisters (vent sorb) in order to use them as an alternate control device for benzene storage vessels. The carbon canisters will control only breathing losses (benzene storage vessels turnovers are zero, so working losses are zero).

CREDIBLE EVIDENCE:

This permit contains provisions which require that specific test methods, monitoring or recordkeeping be used as a demonstration of compliance with permit limits. On February 24, 1997, the U.S. EPA promulgated revisions to the following federal regulations: 40 CFR Part 51, Sec. 51.212; 40 CFR Part 52, Sec. 52.12; 40 CFR Part 52, Sec. 52.30; 40 CFR Part 60, Sec. 60.11 and 40 CFR Part 61, Sec. 61.12, that allow the use of credible evidence to establish compliance with applicable requirements. At the issuance of this permit, Kentucky has only adopted the provisions of 40 CFR Part 60, Sec. 60.11 and 40 CFR Part 61, Sec. 61.12 into its air quality regulations.